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^{226}Ra determination via the rate of ^{222}Rn ingrowth with the Radium Delayed Coincidence Counter (RaDeCC)

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Abstract

We present a new method to determine ^{226}Ra in aqueous environmental samples, based on the rate of ingrowth of ^{222}Rn from ^{226}Ra , using the radium delayed coincidence counter (RaDeCC). We use the same instrument setup that is used for the determination of ^{223}Ra and ^{224}Ra . In contrast to methods published earlier, the approach does not require a modification of the counting equipment, counting separately for ^{226}Ra , or waiting for radioactive equilibrium. We show that the calibration works from as low as 10 dpm (0.166 Bq) per sample, up to more than 1000 dpm (16.7 Bq). Although uncertainties are larger (typically around 10%) than reported uncertainties for γ counting, liquid scintillation, or mass spectrometry at comparable activities, the simple setup, low cost, and robustness of the method make it a useful approach for underway measurements, combinations with short-lived radium isotopes, or monitoring purposes when limited funding or infrastructure is available.

^{226}Ra , a naturally occurring isotope of the ^{238}U -series with a half-life of 1600 years, is a tracer of considerable interest in studies of the marine environment, estuarine systems, and submarine groundwater discharge (Burnett et al. 2006; Moore 2003). It can also be of radiation safety concern, e.g., in the vicinity of offshore oil production facilities (Moatar et al.

2010). The main source of ^{226}Ra in the oceans are sediments, and because of its low particle reactivity in saline waters, it is a valuable water mass tracer of its own. ^{226}Ra is also used in combination with the other three radium isotopes (^{223}Ra , ^{224}Ra , and ^{228}Ra), using their isotope ratios. Radium isotopes store valuable information on mixing in aqueous systems, and the fact that four isotopes with different half-lives from 3.66 days to 1600 years exist, makes the so-called radium quartet unique in its potential to study mixing and submarine groundwater discharge on a wide range of time scales (Charette et al. 2001; Ku and Luo 2008; Rama and Moore 1996). The full potential of the radium quartet has only become available recently, after the development of the Radium Delayed Coincidence Counter (RaDeCC), which allowed the simple and reliable determination of ^{223}Ra and ^{224}Ra (Moore 2008; Moore and Arnold 1996).

The RaDeCC method is based on the filtration of a water sample through a Mn-fiber, which quantitatively extracts radium isotopes from the solution. Then, the Mn-fiber, on which radium isotopes are adsorbed, is placed in the RaDeCC system. As the decay chains of all natural radium isotopes include an isotope of radon, this gas emanates from the Mn-fiber and is continuously transferred to a scintillation cham-

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ber, in which the subsequent decays are detected. The different half-lives of the decay products of ^{223}Ra and ^{224}Ra allow the discrimination of these nuclides based on an electronic detection gateway pioneered in 1963 (Giffin et al. 1963). All events, including decays that cannot be attributed to either the ^{223}Ra chain or the ^{224}Ra chain, are counted in a specific channel.

So far, measurements with the RaDeCC counter in standard configuration could not provide ^{226}Ra values, which made a separate measurement with different equipment necessary. Most commonly, this additional method is γ -spectrometry, which also requires further processing of the sample (i.e., pre-concentrating radium by co-precipitation with Ba, or ashing the Mn-fibers: see e.g., Charette et al. 2001; Moore et al. 1995). Increasingly, mass spectrometry is applied to measure ^{226}Ra (Bourquin et al. 2011; Foster et al. 2004). Further alternatives are given in liquid scintillation systems, or after a waiting period for ^{222}Rn ingrowth, a RaDeCC system with a substantially modified sample holding cell (Waska et al. 2008). Several of these methods have been evaluated as part of a recent intercalibration study in the context of the international GEOT-RACES exercise, highlighting the need for common reference materials (Charette et al. 2012). A comparison of several methods based on Mn-fiber can be found in Peterson et al. (2009).

Here, we present a new evaluation method that allows extracting information on the ^{226}Ra concentration from the RaDeCC channel that records total counts, without modifying the analytical setup that is used for ^{223}Ra or ^{224}Ra . The concept is based on the increasing concentration of ^{222}Rn from the ^{226}Ra present in the sample. In a flushed counting system, initially no ^{222}Rn is present, and all counts observed in the “total channel” are due to daughters of ^{224}Ra and ^{223}Ra . Once the system is closed, any increase of the counting rate, or trend, in this “total channel” over time is then due to ^{222}Rn gas building up from ^{226}Ra , the rate of increase in ^{222}Rn being directly related to ^{226}Ra activity. We exploit this relationship to obtain ^{226}Ra values, without waiting for a radioactive equilibrium. Indeed, we obtain the values just together with a measurement of ^{223}Ra and ^{224}Ra , without need for a separate analysis. The method can even be applied to existing runs for short-lived Ra isotopes, if ^{224}Ra and ^{223}Ra are low enough, without re-analyzing the fiber. It requires only minimal infrastructure, making it a very cost-efficient alternative for ^{226}Ra analysis.

Methods

Equipment

The analytical equipment used here was the Radium Delayed Coincidence Counting (RaDeCC) instrument, supplied by Scientific Computer Instruments, as described in Moore and Arnold (1996). It consists essentially of (1) a large-volume scintillation cell, connected to a photomultiplier to detect radioactive decay events, (2) an electronic gateway system, which registers counts and splits the registered events into different channels, depending on the time elapsed until the next event happens, and (3) a pump, which continuously

pumps helium through the sample (on an acrylic fiber coated with manganese dioxide, Mn fiber), and subsequently through the scintillation chamber. Our study includes data from three different laboratories: the University of Edinburgh, the Universitat Autònoma de Barcelona, and the Université Paul Sabatier/LEGOS Toulouse. γ counting for ^{226}Ra was done on planar detectors (Université Paul Sabatier, Toulouse) and on a well-type high purity Ge detector (Universitat Autònoma de Barcelona). ^{226}Ra determinations via MC-ICP-MS were performed at the University of Oxford. Sampling took place as described in Moore (2008), using Mn-fiber supplied by Scientific Computer Instruments. Samples were rinsed with deionised or distilled water, partially dried (Sun and Torgersen 1998) and stored in resealable plastic bags. They were placed in the cartridges of the RaDeCC system only before measurements.

Principle

Briefly, the RaDeCC system records decay events in three different channels, depending on the time elapsed between two subsequent signals, which reflect the half-lives of decay products in the relative decay chains (Moore and Arnold 1996). One channel counts decay events from the ^{223}Ra decay chain; a second channel counts events from the decay chain following ^{224}Ra ; and the third channel (“total”) records basically all events, independent of previous or subsequent events. Therefore, each signal in the ^{223}Ra or ^{224}Ra channels is accompanied by events in the “total” channel, but not all events in the “total” channel are due to ^{223}Ra or ^{224}Ra decay products. Counts in the total channel have been known to build up over time during a run, due to ingrowth of ^{222}Rn from ^{226}Ra , which is also present on the fiber, up to activities that start to affect counts in the ^{223}Ra and ^{224}Ra channels due to chance coincidence events. Here, we exploit this ingrowth to determine the ^{226}Ra activity in the sample. Rather than waiting for equilibrium, which is quite demanding in terms of instrument time and requirements for gas tightness of the setup (Waska et al. 2008), we only use the first 1000 min of a run. During this relatively short period, the increase on the counting rate of ^{222}Rn can be approximated as a linear trend, as the influence of ^{222}Rn decay term is small (Fig. 1).

Theoretical ^{226}Ra efficiency in the total channel

What rate of increase in counts per minute (cpm) from ^{226}Ra should we expect on a RaDeCC system? The facts to consider are (1) the activity of ^{226}Ra on a sample (fiber), (2) the ingrowth of ^{222}Rn , (3) the desorption efficiency of ^{222}Rn from the fiber, (4) the fraction of detector volume relative to the entire system volume, (5) detector efficiency, and (6) number of subsequent decay events related to a previous ^{222}Rn atom decay.

The calculation differs slightly from the calculation for the other two channels as given in Moore and Arnold (1996), as we do not have to consider decay on the way from the fiber to the detector because of the long half-life of ^{222}Rn , and we don't have to include probabilities of coincidences of two events, like for the ^{224}Ra and the ^{223}Ra channel.

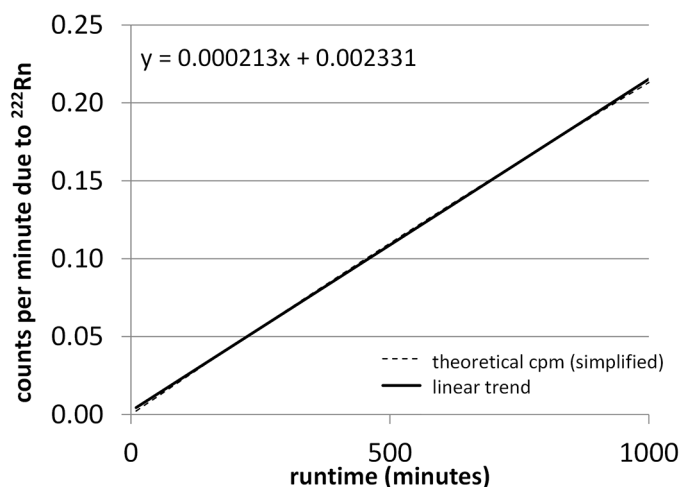


Fig. 1. Theoretical evolution of the ^{222}Rn signal due to ^{226}Ra for an activity of 1 dpm in the “total channel” in a closed system, considering typical efficiencies of a RaDeCC system. During the first 1000 min, ^{222}Rn reaches less than 12% of the ^{226}Ra activity (not shown here), and the decay term is almost negligible. Therefore, ingrowth is nearly linear, and a linear regression (solid line) of ^{222}Rn activity versus time (trend) is almost indistinguishable from the actual exponential ingrowth (dashed line).

To calculate the expected trend in count rate due to ^{222}Rn ingrowth, we assume a starting ^{226}Ra activity of 1 dpm. Ingrowth is calculated as $1 - e^{-\lambda t}$, where λ is the decay constant of ^{222}Rn , and t is the time elapsed since starting the analysis (assuming a starting value of 0 dpm ^{222}Rn). We assume the desorption of ^{222}Rn to be quantitative over the time available between generation by ^{226}Ra and subsequent decay, as supported e.g., by the results of Butts et al. (1988). The fraction of detector volume relative to total system volume is assumed to be 0.77, following Moore and Arnold (1996). We assume a detector efficiency of 0.78 as a starting point, also following Moore and Arnold (1996). Finally, we assume each ^{222}Rn atom to generate three subsequent α -decay events, modeled in approximation as having the same probability, which triples the probability to detect a decay due to ^{222}Rn in the theoretical example. Please note that real measurements will deviate by different detection efficiencies for the daughter nuclides, variable cell characteristics, and a time lag between ^{222}Rn and the decay of daughter isotopes due to the half-lives of intermediate products. This will later be reflected in actual calibration factors, but the assumptions that lead to Eq. 1 are a good approximation to understand the expected cell behavior.

$$\text{expected count rate} = (1 - e^{-\lambda t}) \times 0.77 \times 0.78 \times 3 \quad (1)$$

$\lambda = 0.000125893$, t = time elapsed since start of measurement.

Using the starting parameters outlined above, we determine an expected increase of 0.000213 cpm/dpm over the first 1000 min (Fig. 1).

It should be considered that system efficiencies may vary, e.g., values in Moore (2008) are slightly higher than those given in Moore and Arnold (1996), and so does the ratio of detector volume over total volume, so efficiencies should be expected to differ slightly between systems, depending on the geometry and the detector efficiency. The experimental trends in ^{222}Rn will be compared with the theoretical value of 0.000213 below, after having introduced the required data processing of raw counts from the total channel in the following section.

Evaluation of the counting results

Having shown the expected direct relationship between ^{226}Ra concentration and ^{222}Rn ingrowth in a closed system (Fig. 1), the aim of our calculation is to determine the trend of ^{222}Rn in the RaDeCC “total channel” from a measurement. Whereas most of the signal seen in this channel is indeed due to ^{222}Rn , a few minor contributions from the other Rn isotopes (i.e., ^{220}Rn and ^{219}Rn) should also be considered, especially as their activity may be decreasing over time. Therefore, before calculating the trend, we need to subtract the contributions from ^{220}Rn and ^{219}Rn and their daughters to the “total channel.” These, in turn, first have to be corrected for chance coincidence counts in the respective channels, as they are actually due to ^{222}Rn and should not be subtracted. Our calculation follows closely the approach outlined in Moore and Arnold (1996) and Garcia-Solsona et al. (2008), extending it to the “total” channel, resulting in a value of corrected “total” counts per minute ($\text{corr}_{\text{total}}$) for each counting cycle (10 min cycles in our case) in a 1000 min (or similar) counting period. From these data points, a linear regression over time (trend) is then obtained. The total counting period may be shortened, if high activities command shorter measurements.

The calculation starts with the determination of the chance coincidence count rate in the ^{220}Rn channel:

$$Y_{220} = \frac{(\text{cpm}_{\text{total}} - \text{cpm}_{220} - \text{cpm}_{219})^2 \times 0.01}{1 - (\text{cpm}_{\text{total}} - \text{cpm}_{220} - \text{cpm}_{219}) \times 0.01} \quad (2)$$

Y_{220} , expected count rate (counts per minute) due to chance coincidence events in the ^{220}Rn channel; $\text{cpm}_{\text{total}}$, measured count rate in the “total” channel; cpm_{220} , measured count rate in the ^{220}Rn channel; cpm_{219} , measured count rate in the ^{219}Rn channel.

The corrected count rate for the “ ^{220}Rn channel,” which is the fraction of the counts that can actually be attributed to ^{220}Rn , can then be calculated. The correction will increase as counting time elapses, as ^{222}Rn , and consequently, chance coincidence events in the “ ^{220}Rn channel” build up. The corrected ^{220}Rn count rate without chance coincidence contribution is calculated as

$$\text{corr}_{220} = \text{cpm}_{220} - Y_{220} \quad (3)$$

The term corr_{220} is, in turn, part of Eq. 3, which determines the chance coincidence fraction for the “²¹⁹Rn channel.”

$$Y_{219} = \frac{(cpm_{\text{total}} - \text{corr}_{220} - cpm_{219})^2 \times 0.0000935}{1 - (cpm_{\text{total}} - \text{corr}_{220} - cpm_{219}) \times 0.0000935} \quad (4)$$

Y_{219} , expected cpm due to chance coincidence events in the “²¹⁹Rn channel.”

For the “²¹⁹Rn channel,” we do not only need to consider chance coincidence events (which are less likely due to the shorter opening time of the electronic gate), but we also have to consider that some ²²⁰Rn counts occur while the ²¹⁹Rn gate is open, which is why the equation for final_{219} comprises an additional term compared with the calculation of corr_{220} . The actual value for the constant (0.0255) in this equation will depend on the settings of the electronic gates. The ²¹⁹Rn count rate without chance coincidence events and without ²²⁰Rn-related counts is calculated as

$$\text{final}_{219} = cpm_{219} - Y_{219} - \text{corr}_{220} \times 0.0255 \quad (5)$$

Just like a fraction of ²²⁰Rn (and subsequent) decays is observed in the “²¹⁹Rn channel,” a fraction of ²¹⁹Rn related decays is detected in the “²²⁰Rn channel,” which is why we need to determine the final ²²⁰Rn count rate without chance coincidence events and without ²¹⁹Rn-related counts:

$$\text{final}_{220} = \frac{\text{corr}_{220} - (1.6 \times \text{corr}_{219})^2 \times 0.01}{1 - (1.6 \times \text{corr}_{219}) \times 0.01} \quad (6)$$

With the value from Eqs. 4 and 5, we can finally correct the count rate in the “total channel” for events actually due to ²¹⁹Rn and ²²⁰Rn, to have just ²²²Rn and subsequent counts. As each event in the ²¹⁹Rn or ²²⁰Rn channels is associated with two counts in the “total channel,” the respective values are multiplied by 2 to calculate the corrected total counts. The “total” count rate without ²¹⁹Rn- and ²²⁰Rn-related counts or the count rate that can be attributed to ²²²Rn is calculated as

$$\text{corr}_{\text{total}} = cpm_{\text{total}} - 2 \times \text{final}_{219} - 2 \times \text{final}_{220} \quad (7)$$

This set of calculations is applied to each counting cycle to obtain series of values for 1000 min counting time. If there is ²²⁶Ra present in the sample, the count rate will increase over time. The set of $\text{corr}_{\text{total}}$ values, which represents the corrected counts from the “total channel,” is used to calculate the slope of these counts over time. This slope is then a direct measure of the activity of ²²⁶Ra absorbed on the Mn fiber. It should be

noted that these corrections have a minor effect on the overall quality of the ²²⁶Ra values, as the correction is only small, except when high ²²⁶Ra activities are measured (>20 dpm of ²²⁶Ra per Mn-fiber). We provide a spreadsheet in Microsoft Excel format with this article, which allows performing the calculations from Eqs. 2-7 by pasting a raw RaDeCC spreadsheet in the appropriate columns (see Web Appendix).

In the next step, we will calibrate the actual ²²⁶Ra activity on a Mn-fiber against the instrument-specific $\text{corr}_{\text{total}}$ -slope for different activities, using the values from Eq. 7.

Calibration

To calibrate the response of the system, a set of Mn fibers (25 g dry weight each) containing nominally 5, 10, 15, 25, and 50 dpm of ²²⁶Ra was prepared at Alfred-Wegener-Institute (AWI), Bremerhaven. From a stock solution containing 530 dpm·g⁻¹ ²²⁶Ra in 0.5 M HCl, the respective amounts were added to a glass beaker, and 200 mL ultrapure water was added so each Mn fiber could be entirely submerged. Before adding the Mn fiber, pH was raised to ~9 by adding sodium carbonate (Na₂CO₃), as monitored with a pH indicator strip. Then the Mn fiber was submerged in the spike solution for approximately 10 min. After taking out the fiber, it was squeezed dry and rinsed three times with ultrapure water, analogue to a sample. The resulting ²²⁶Ra calibration series on Mn fiber was transferred to regular cartridges as used for sampling and counting of short-lived Ra-isotopes, and stored damp (but not specifically sealed for gas loss).

We then analyzed each standard fiber in each counter of the Edinburgh 4-counter system, calculated $\text{corr}_{\text{total}}$ according to the equations outlined above for each measurement cycle (here 10 min), and determined the resulting trend (slope) in $\text{corr}_{\text{total}}$ for each concentration on each counter. The increasing trend in $\text{corr}_{\text{total}}$ with increasing ²²⁶Ra concentrations (shown in Fig. 2) allows us to calculate the response of an individual system to a given amount of radium present on the fiber, or a specific calibration factor.

The result of the calibration for four different counters (University of Edinburgh system) with standards is shown in Fig. 2. For all detectors, an increase in ²²⁶Ra concentration on the Mn-fiber leads to a linear increase in the trend of $\text{corr}_{\text{total}}$. This test resulted in similar calibration values for all Edinburgh systems: 0.000186, 0.000190, 0.000155, and 0.000141 cpm·dpm⁻¹ for the four detectors used here. These values agree reasonably well with the theoretical trend expected from the previous section (0.000213 cpm/dpm). After describing the methods in more detail, we will compare further experimental instrument responses to the theoretical value, using real samples that had been analyzed for ²²⁶Ra by an independent method.

Measurement and possible sources of error

For a measurement of ²²⁶Ra with the RaDeCC, the system is first flushed well with air to remove moisture and traces from previous measurements, then it is flushed with helium of at least industrial grade quality. The latter happens to remove

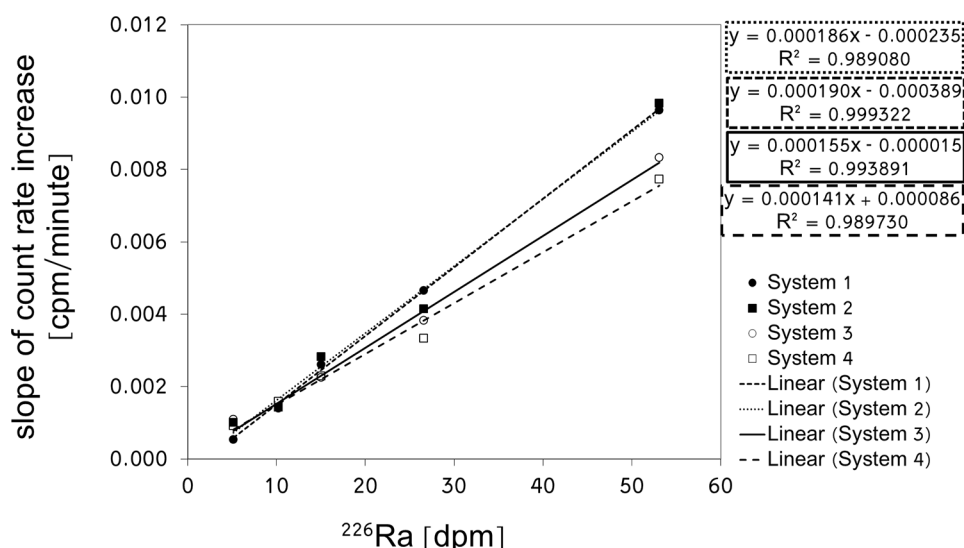


Fig. 2. Calibration of four different RaDeCC counters (Edinburgh). The x-axis represents the amount of ^{226}Ra standard present on a Mn fiber. The y-axis displays the slope of the increase in count rate in the respective “total channel.”

any ^{222}Rn that has built up from previous measurements. Then the standard (or sample) on fiber with appropriate moisture content (Sun and Torgersen 1998) is placed in a closed recirculated helium stream according to Moore and Arnold (1996). Counts are monitored in the “ ^{219}Rn channel” (= ^{223}Ra), the “ ^{220}Rn channel” (= ^{224}Ra), and the “total channel,” in 10 min cycles, for 1000 min.

It should be noted that three sources for systematic error have to be considered. One is a loss of Rn (and He) during counting. Such a leak is a problem for any Ra isotope measurement on the RaDeCC counter, as Rn losses imply an underestimation of the Ra results, and efficiencies in air differ considerably from efficiencies in He (Moore 2008). During the measurement, changes in gas flow rate are a good indicator for gas loss. After the measurement, such an event can usually be seen in the data as a clear break in the linear increase of total counts (Fig. 3c).

Another problem (possibly encountered after determining cell efficiencies for ^{224}Ra , or after counting high levels of ^{226}Ra) is a slowly decreasing background in the “total channel,” starting from relatively high levels, presumably due to $^{212}\text{Pb}/^{212}\text{Bi}$ daughter ^{212}Po (from ^{224}Ra), or supported ^{214}Po (from ^{226}Ra) that has accumulated in the cell from a previous measurement. Again, this problem can be identified in a deviation from linearity in the ^{222}Rn increase over time (Fig. 3d). The half-life of ^{212}Pb is 10.64 h, so it is recommended to wait for 1–2 d after counting high-activity ^{224}Ra samples. High residual activities from ^{226}Ra daughters can usually be encountered by discarding the first 150 min of a run. The first two problems can easily be ruled out when visually checking each sample run in a scatterplot of $\text{corr}_{\text{total}}$ versus time, which should be done while determining the slope for each measurement.

The third source of error is elevated values of short-lived Ra,

in particular ^{224}Ra , which indirectly leads to an increase in the total channel due to ^{214}Po . The latter effect cannot easily be separated from increasing counts due to ^{222}Rn , so we recommend using a measurement after decay of the short-lived Ra isotopes for the evaluation of ^{226}Ra . Samples of >1 cpm ^{224}Ra should generally be considered problematic for ^{226}Ra measurement via the RaDeCC, unless a suitable correction for $^{212}\text{Pb}/^{212}\text{Bi}/^{212}\text{Po}$ ingrowth is found.

Uncertainty calculation

As with all counting techniques, the uncertainty of the measurement is, in first approximation, mainly determined as a function of the number of counts. However, the results here are determined through the trend of the “total” count rate increase, rather than just the number of counts, and thus the uncertainty of the results corresponds also to the uncertainty associated to the trend.

We describe the linear trend in the data by a general equation

$$y = mx + b \quad (8)$$

in which y is the count rate $\text{corr}_{\text{total}}$, x is elapsed counting time, b is the offset at $x = 0$, and m is the sample-specific slope describing the increase over time (trend). The uncertainty in m , s_m , is then the best description of uncertainty for the measurement of ^{226}Ra , rather than the correlation coefficient R^2 . Even with poor R^2 , the trend m in the data is usually robust, as the scatter leading to a lower R^2 is purely statistical in nature, and a large number of cycles (typically $n = 100$) implies that the regression does not depend very much on individual values. This means that while we cannot predict very well a specific value for an individual measurement cycle due to the stochastic nature of radioactive decay, we can determine the

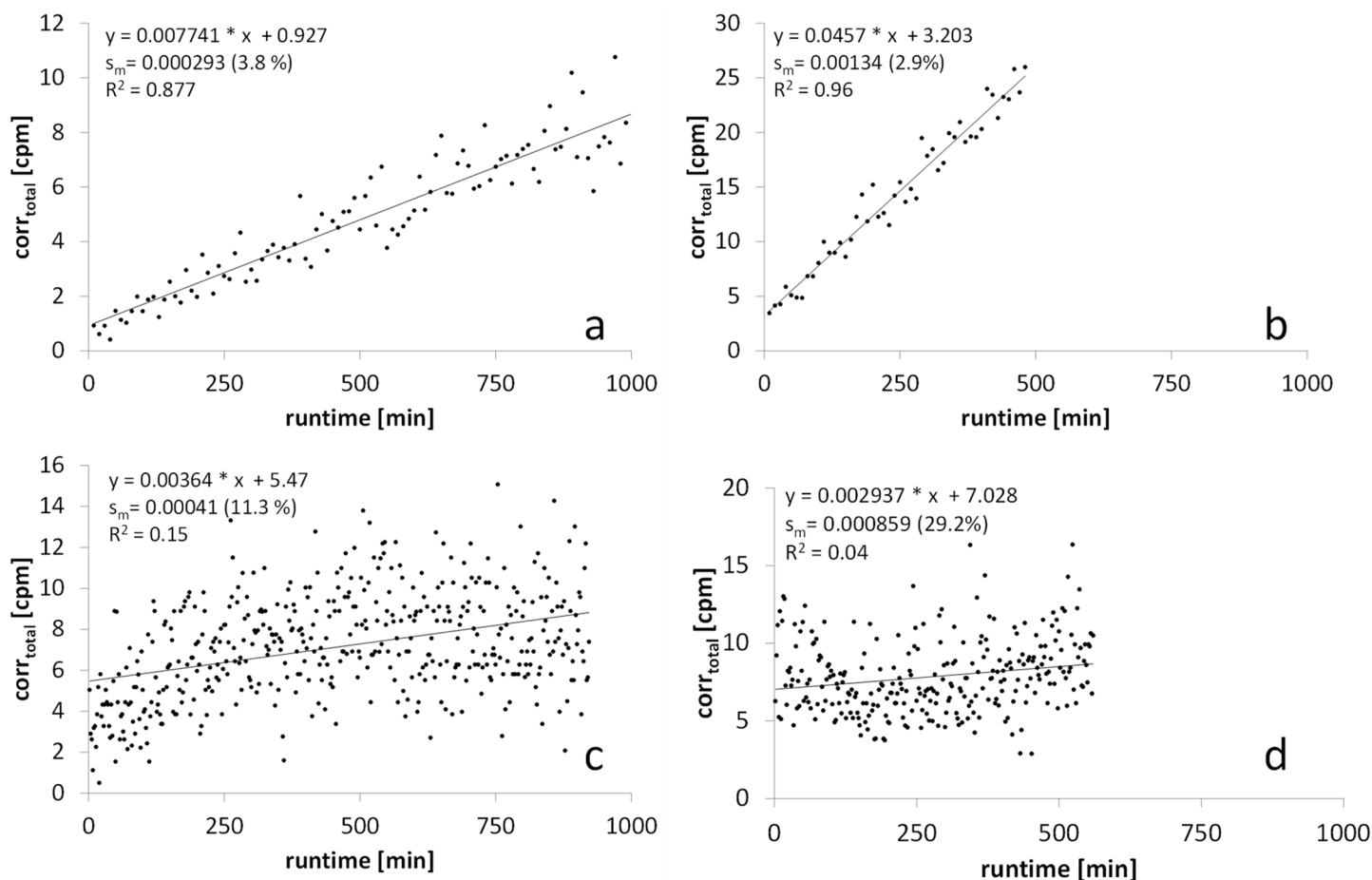


Fig. 3. Examples of observed trends in $\text{corr}_{\text{total}}$. Panel a: Typical ingrowth in $\text{corr}_{\text{total}}$ here for 50 dpm ^{226}Ra on the fiber (10-min cycles). Panel b: An example of a high activity sample with shortened measurement interval (293 dpm on the fiber, 10-min cycles). Panel c: A sample with a change in slope due to gas loss (2-min cycles). Not suitable for evaluation. Panel d: A sample with high background from a previous measurement. Not suitable for evaluation, as all potentially affected measurement cycles would have to be excluded with certainty (2-min cycles).

trend very reliably. From a practical perspective, we recommend the additional determination of the analytical uncertainty by measuring replicates of samples and standards, ideally reference materials as well.

Assessment

Determining the range of the method

To assess the applicability of the method to existing measurements, and to establish the range of suitable activities, we first chose a set of $^{223}\text{Ra}/^{224}\text{Ra}$ Mn fiber samples with existing independent ^{226}Ra measurements (by γ -spectrometry) for comparison, covering a wide range of activities (2.4 to 2200 dpm) [details on most of the sampling sites and methodology can be found in Rodellas et al. (2012), Annett et al. (2013), Van Beek et al. (2010)]. In this sample set, samples were counted on different RaDeCC detectors, and the resulting trends have not been calibrated for different detector efficiencies, so we can compare the observed trends in $\text{corr}_{\text{total}}$ with the simplified theoretical value of 0.000213 cpm/dpm. The lack of a detector-specific calibration in the graph contributes to the

observed scatter in the results. However, this can also be seen as a test for the robustness of the method.

We find that the relation between ^{226}Ra from an independent analysis and the trend of $\text{corr}_{\text{total}}$ on the RaDeCC systems is strictly linear and quite close between 10 dpm and 2000 dpm/sample (see Fig. 4). In the log/log plot covering the full range of activities (Fig. 4, righthand panel), it can be seen that samples below 10 dpm have a less close correlation in this sample set, which is mainly due to the counting error, as counting intervals are often shorter than 1000 min for most of these samples, and it may in this case be reinforced by the absence of a detector-specific calibration and by including values from three different laboratories. However, the correlation is overall very satisfying, with $R^2 = 0.97$ for all values across all participating laboratories, with an average slope of 0.000188 $\text{corr}_{\text{total}}/\text{dpm}$ (theoretical slope for 78% detector efficiency: 0.000213; one individual system actually up to 0.000230).

To investigate the statistical uncertainty in the ^{222}Rn trend, we present the observed relative error from the dataset above in relation to the ^{226}Ra concentration (Fig. 5).

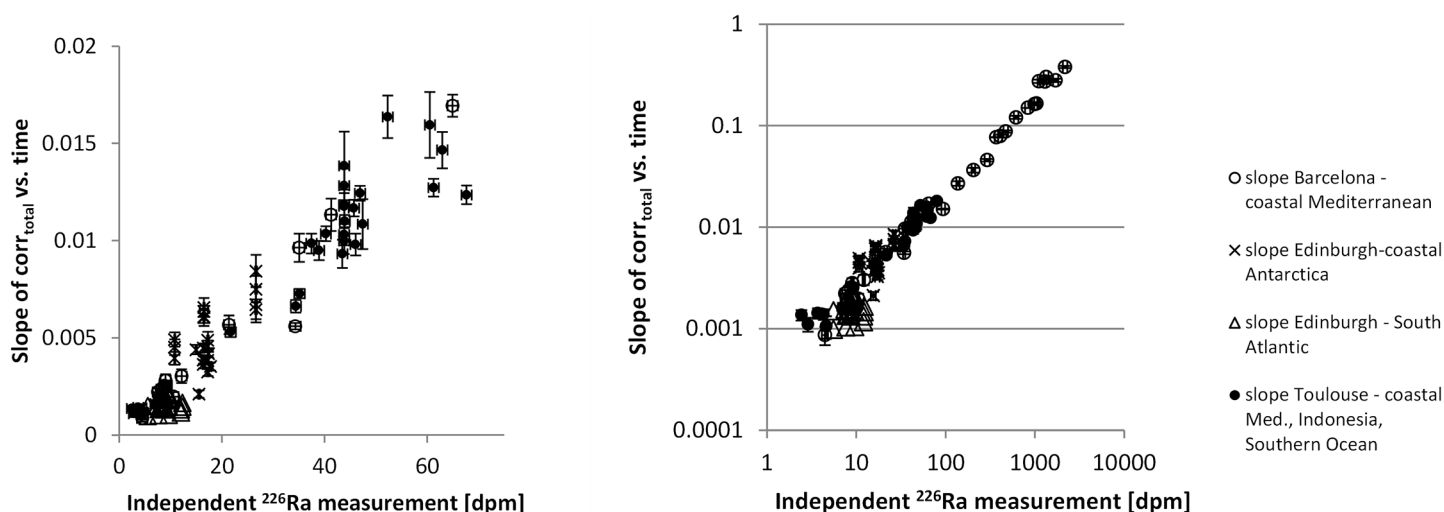


Fig. 4. In the left panel, the measured trends in $\text{corr}_{\text{total}}$ in RaDeCC systems from three different laboratories are shown (UABarcelona, U Edinburgh, U Paul Sabatier/LEGOS Toulouse), for actual water samples covering ^{226}Ra concentrations from 2.4 to 75 dpm, as determined independently by γ -spectrometry or MC-ICP-MS. No correction for system efficiency (calibration factor) was applied. The right panel shows the same dataset in log scale, including values up to >2000 dpm ($n = 114$) ^{226}Ra . The error bars show the analytical error (1σ) for ^{226}Ra (γ -spectrometry, MC-ICP-MS) and the uncertainty in the trend of $\text{corr}_{\text{total}}$ (s_m) for the y-axis.

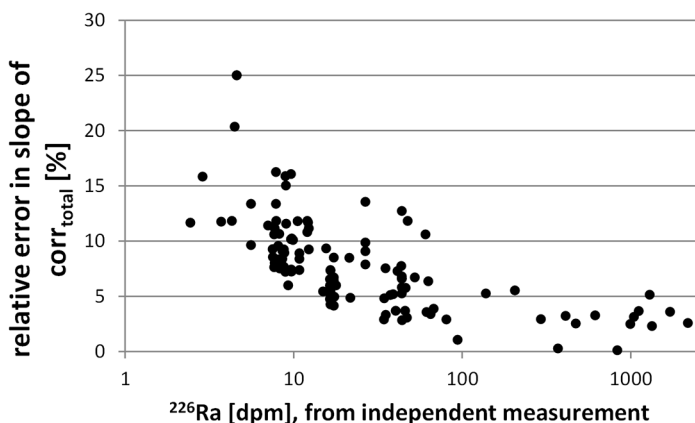


Fig. 5. Relative error in slope of $\text{corr}_{\text{total}}$ versus ^{226}Ra activity. The uncertainties reflect purely the error in the slope (s_m) and do not take into account errors from the uncertainty of the calibration.

We observe a general decrease of statistical uncertainty with increasing ^{226}Ra activity, as expected. We find that values above 10 dpm have relative errors of less than 15% in this example. Uncertainties of less than 15% for even lower activities around 5 dpm suggest that it may be possible to obtain values with a certain precision for activities < 10 dpm in certain cases (well calibrated system; no influence from other isotopes; constant conditions).

Radium adsorption efficiency determination in the South Atlantic (GEOTRACES GA10E) and a GEOTRACES intercalibration sample

As an additional test for the new method, we applied the technique to a set of samples from the South Atlantic. This set

of large-volume (approx. 100 L) samples of water was collected from the upper 400 m in a transect from Cape Town to Gough Island along the 40°S in the Atlantic Ocean during the British UK GEOTRACES cruise GA10E onboard RRS *Discovery* in 2010. The samples were passed through Mn-fiber at a flow rate < 0.5 L/min to quantitatively extract the Ra, following Moore and Arnold (1996) and Moore (2008).

In parallel for 12 of the large-volume Ra samples reported here, 500 mL samples were taken, of which 200 mL were used to determine the ^{226}Ra concentrations independently by isotope dilution on a multicollector- ICP-MS at Oxford University, following the methods in Hsieh and Henderson (2011). The results are reported in Hsieh et al. (in prep.). For the remaining samples without an actual MC-ICP-MS value, we have used interpolated estimates in the calculation (as indicated in Table 1), as variations in ^{226}Ra in this location can be expected to be relatively small. Therefore, we can compare the results on the ^{226}Ra concentrations obtained from each of the large-volume Mn-fiber samples with those independently determined, which make them a suitable set to test the method outlined in this work. With typical activities around 10 dpm-100 kg^{-1} ^{226}Ra for near surface waters in this part of the South Atlantic (Ku and Lin 1976), and sample volumes of around 100 kg, most samples have an absolute activity of around 10 dpm, placing them at the lower end of the suitable activity range, and elevated uncertainties are to be expected. The data are presented in Table 1.

We only show the 16 samples that were counted twice, once shortly after sampling on board, and a second time when back in the home lab (see Table 1). Short-lived Ra isotopes were low, even shortly after sampling. When averaging the

Table 1. Comparison of ^{226}Ra activity determined via MC-ICP-MS (200 mL sample), and ^{226}Ra via RaDeCC (on Mn fiber). Whereas the scatter is large due to relatively low ^{226}Ra activities for the RaDeCC-method, no systematic offset is found, and averaging of two subsequent runs can be used to improve statistics.

Sample ID	sample mass	MC-ICP-MS on discrete 200 mL sample		RaDeCC - 1st run			RaDeCC- 2nd run			RaDeCC Average 2 runs		
	[kg]	²²⁶ Ra [dpm/100kg]	±1 s	²²⁶ Ra [dpm/100kg]	±1 s	Recovery [%]	²²⁶ Ra [dpm/100kg]	±1 s	Recovery [%]	²²⁶ Ra [dpm/100]	Recovery [%]	
Test	105	8.3	0.2	12.3	1.2	148	8.9	1.0	108	10.6	128	
St1_fish	107	8.3	0.2	8.7	1.4	105	12.2	1.0	146	10.4	126	
St1_50m	89	8.6	0.2	10.7	0.8	125	6.1	0.7	71	8.4	98	
St1_100m	102	9.4	0.2	5.5	0.9	58	7.7	0.9	82	6.6	70	
St1_400m	104	11.6	0.2	7.9	1.0	68	9.1	1.1	78	8.5	73	
St2_fish	116	8.3	0.2	10.7	0.9	129	9.4	0.7	113	10.0	121	
St2_50m	68	8.2	0.2	11.5	1.1	140	7.7	1.1	94	9.6	117	
St2_100m	92	8.4	0.2	11.3	1.1	135	9.5	1.1	113	10.4	124	
St2_400m	92	9.3	0.2	12.8	1.3	138	9.4	1.0	101	11.1	120	
Super1Fish	89	9.1	0.2	9.3	1.0	102	8.2	0.7	90	8.7	96	
St4_fish	106	9.2	0.2	12.8	1.2	139	7.3	0.8	79	10.0	109	
St4_700m	92	13.4	0.3	10.3	1.2	77	9.7	1.1	72	10.0	74	
St5_fish	94	9 est		12.4	1.4	138	8.2	0.9	92	10.3	115	
St5_50m	75	11 est		10.2	1.3	92	7.6	0.9	69	8.9	81	
St5_400m	100	11 est		10.7	1.1	97	13.8	1.4	126	12.3	112	
St7_Fish	104	9 est		8.8	0.8	98	11.3	1.0	126	10.1	112	
					Av.	112		Av.	97		Av.	105
					± 1 s	29		± 1 s	23		± 1 s	20

two counts, we determine an average recovery with the RaDeCC method of $105 \pm 20\%$ compared with MC-ICP-MS, demonstrating a generally good agreement even for relatively low activities. We also find that the error associated with individual ^{226}Ra determinations by the ingrowth method can be decreased by including replicate analyses.

In addition to the examples above, we applied the new method to an existing intercalibration sample, station 3 from Charette et al. (2012). The available amount was very low, 8.34 kg, which were extracted on Mn fiber. The ^{226}Ra activity of the sample is reported in Charette et al. (2012) as 11.6–24.3 dpm/100 kg (95% Conf. Int.), and the ICP-MS value of the sample is 14.6 ± 0.3 dpm/100 kg. Assuming that the existing MC-ICP-MS measurement is the best estimate, we only had 1.22 dpm ^{226}Ra available for the test, which is considerably below the proposed working range of the method. The evaluation of two 1000 min runs yielded 26.6 ± 5.7 (1 s) and 27.1 ± 7.7 (1 s) dpm/100 kg, respectively. Given the very low absolute sample amount below the specification of the method, we consider this a reasonable agreement.

Discussion and comments

Our results from the calibration of four detectors and several actual examples of environmental samples from three different laboratories confirm that the ingrowth of ^{222}Rn as measured in the closed system of a RaDeCC-system is a reliable measure for the activity of ^{226}Ra on Mn fiber. We find that the method works well in a range from 10–2000 dpm. The measurement of slightly lower activities might be achieved by increasing the number of replicates, or by choosing longer measurement cycles. Uncertainties for individual measurements are in the order of 10% to 20% for activities from 10–20 dpm, but replicate analyses of the same sample allow reducing the uncertainty further. At the current stage of method development, sample volumes for a typical coastal environment with 10 dpm/100 kg ^{226}Ra should be not less than 100 L. The main advantage of the method is its simplicity, combined with the fact that an analysis of ^{223}Ra and ^{224}Ra with the RaDeCC system can be evaluated for ^{226}Ra , without requiring a modification of the setup. Moreover, the data record of measurements previously done with the RaDeCC

system (determination of ^{223}Ra , ^{224}Ra , or ^{228}Th), allow re-evaluating the existing data to obtain information on ^{226}Ra at no extra costs. It should be noted that the principle of our evaluation can be extended to other parent-daughter radionuclide systems, when waiting for a secular equilibrium is inconvenient, e.g., to ^{228}Ra via ^{228}Th ingrowth.

We do not believe that the method presented here is a replacement for existing more precise methods, but a valuable complementation of the analytical tools for ^{226}Ra . For laboratories with an existing RaDeCC-facility, a very simple assessment of the new method can be conducted by re-evaluating existing analytical records with the provided spreadsheet, and assuming a slope/ ^{226}Ra conversion factor of 0.00019. Quality checks of the sample runs (no gas leaks, no elevated background at beginning of measurement, low ^{223}Ra and ^{224}Ra) are essential for the successful use of the method. The precision can then be further improved by determining individual efficiencies for the systems, and by measuring replicates.

The method is suitable for determining Mn fiber adsorption efficiencies, if a sufficient number of replicate analyses of the same sample are performed. The values obtained are of adequate precision to decide how to proceed analytically, e.g., determination of required sample volumes for a more precise γ -spectrometric or mass-spectrometric analysis. The method also has a large potential for monitoring purposes in remote areas, as it has very modest requirements for infrastructure. Basically, a sufficiently stable electricity supply, and the availability of helium (industrial quality) are sufficient to set up the system.

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